Review

Recent advances in olefin metathesis by molybdenum and tungsten imido alkylidene complexes

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Abstract

Recent advances in olefin metathesis studies include the preparation of catalysts "in situ," supported catalysts, and tungsten-based catalysts, and observation of molybdacyclobutane complexes, molybdacyclopentane complexes, base-free methylene complexes, and ethylene complexes such as $Mo(N-2,6-Cl_2C_6H_3)(CH_2=CH_2)[rac-Biphen](Et_2O)$.
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Keywords: Olefin metathesis; Molybdenum imido alkylidene complexes; Tungsten imido alkylidene complexes

1. Introduction

In the last 15 years metal-catalyzed olefin metathesis has had a significant impact on polymer chemistry [1–8] and organic synthesis [9–16]. This can be attributed in large part to the development of "well-characterized" or "well-defined" catalysts based on Mo, W, or Ru. A "well-defined" catalyst is one that is: (i) essentially identical to or resembles the active species in terms of metal oxidation state and ligand coordination sphere; (ii) stable enough to be characterized through spectroscopic means and X-ray analysis; and (iii) reacting with some olefin to yield a persistent new alkylidene complex derived from that olefin. Compounds that are well-characterized, and that under some conditions will catalyze the metathesis of olefins (or carry out some other alkylidene-based reaction), but that have not been proven to be essentially identical to the active species for the metathesis reaction, are not well-defined catalysts. They are catalyst precursors, or "precatalysts".

One type of catalyst precursor that played a role in studies concerned with the mechanism of olefin metathesis are low oxidation state tungsten carbene complexes. For example, Casey synthesized $(CO)_5W=CPh_2$ and showed that it reacts with certain olefins in a manner consistent with the metallacyclobutane mechanism [17–20]. The expected new carbene could be detected under certain circumstances, but other products (e.g., cyclopropanes) were also observed, and metathesis products were formed only in substoichiometric quantities. Katz and co-workers [21–27] showed that certain strained cyclic olefins are polymerized slowly to give the polymers expected from ring-opening metathesis polymerization (ROMP) when the polymerization is initiated by $(CO)_5W=CPh_2$ or even $(CO)_5W=CPh(OMe)$. These investigations (along with many others [5,6]) collectively provided evidence that metal carbenes are involved in olefin metathesis reactions. However, the catalytic ROMP reactions were not conclusive. In spite of the fact that the *initial* carbene complexes were well-characterized, no propagating metal carbene was detected and, therefore, it cannot be concluded that the pentacarbonyl carbene species are responsible for the catalytic reaction. Since no endgroup was identified in the polymer, the nature of the initiating carbene fragment is also in doubt. Moreover, Casey subsequently reported in 1979 that $(CO)_5W=CHPh$ decomposes above $-60\,^\circ C$ and does not yield metathesis products upon reaction with olefins [28]. Therefore, it seems unlikely that Fischer-type W(0) complexes can be propagating species in ROMP reactions in which some catalytic metathesis activity is observed. Almost certainly a small amount of a high oxidation state alkylidene complex (probably an oxo complex) is formed upon decomposition of the Fischer-type carbene complex, and it is the high oxidation state species that is responsible for the metathesis activity.

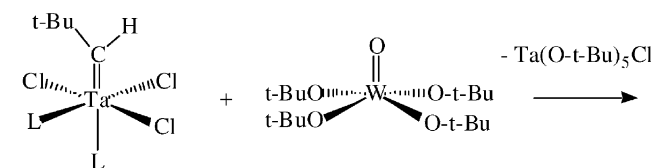* Tel.: +1-617-253-1596; fax: +1-617-253-7670.
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Tantalum played a crucial role in understanding how effective well-defined W and Mo catalysts might be designed that mimic "classical" metathesis catalysts based on W and Mo [5,6]. An attempt to synthesize $Ta(CH_2\text{-}t\text{-Bu})_5$ led to formation of $Ta(CH\text{-}t\text{-Bu})(CH_2\text{-}t\text{-Bu})_3$ (Eq. (1)), the first example of a stable M=CHR complex, through an intramolecular decomposition of intermediate $Ta(CH_2\text{-}t\text{-Bu})_5$ [29]. $Ta(CH\text{-}t\text{-Bu})(CH_2\text{-}t\text{-Bu})_3$ is unusually robust thermally, melting at ∼70 °C and distilling in vacuo.

$$Ta(CH_2CMe_3)_3Cl_2 \xrightarrow[\text{- 2 LiCl - } CMe_4]{\text{2 LiCH}_2CMe_3} \quad \text{(structure)}$$

(1)
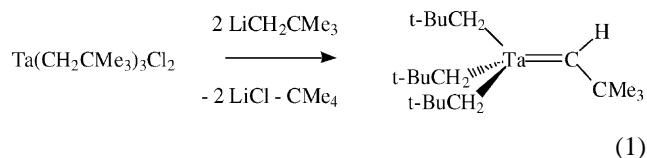
Its robust nature is an excellent example of the degree to which four bulky covalently bound ligands can stabilize even an electronically unsaturated species (here a 10 electron species) toward bimolecular decomposition. This compound is sensitive to oxygen, water, and a variety of functionalities, among them ketones and aldehydes, with which it reacts to yield polymeric $(t\text{-BuCH}_2)_3Ta=O$ and the expected olefin [30]. The importance of this discovery to metathesis was not recognized until 5 years later [31] when it was shown that while $Cl_3(PMe_3)_2Ta=CH\text{-}t\text{-Bu}$ [32] would react with terminal olefins to yield four products of rearrangement of a metallacyclobutane species, $Cl(t\text{-BuO})_2(PMe_3)_2Ta=CH\text{-}t\text{-Bu}$ would react with styrene to produce $Cl(t\text{-BuO})_2(PMe_3)_2Ta=CHPh$, and would initiate the slow metathesis of *cis*-2-pentene (∼35 turnovers) [33,34]. This finding established that d^0 alkylidene species were responsible for olefin metathesis and drew attention to the utility of alkoxide ligands in promoting metathesis. Unfortunately, however, the ethylidene and propylidene intermediates that were formed in the metathesis of *cis*-2-pentene, apparently rearranged readily to give ethylene and propylene, respectively, and therefore could not be observed.

At that time it also was reported that an attempt to prepare $(t\text{-BuO})_4W=CH\text{-}t\text{-Bu}$ in the reaction shown in Eq. (2) led instead to the oxo alkylidene $(PEt_3)_2Cl_2W(O)(CH\text{-}t\text{-Bu})$ quantitatively, the first d^0 alkylidene of tungsten to be reported [35,36]. Since the electron count of

to yield a 16-electron species. Nevertheless, it was found that $W(O)(CH\text{-}t\text{-Bu})Cl_2L_2$ would metathesize terminal and internal olefins very slowly. However, the rate of metathesis was accelerated dramatically in the presence of a trace of $AlCl_3$ [35]. It was in this context that $(PEt_3)_2Cl_2W(O)(CH_2)$ and new alkylidenes that contain β protons, such as $(PEt_3)_2Cl_2W(O)(CHEt)$, were observed for the first time [34]. (A small amount of $[(PEt_3)_2ClW(O)(CH\text{-}t\text{-Bu})][AlCl_4]$ is believed to be responsible for the metathesis of olefins by $(PEt_3)_2Cl_2W(O)(CH\text{-}t\text{-Bu})$ in the presence of a trace of $AlCl_3$). On the basis of these data, the metal oxidation state that is required for efficient metathesis activity was proposed to be W(VI), counting the alkylidene as a dianionic ligand. Although tungsten catalysts that do not contain a second multiply bound ligand in addition to the alkylidene were disclosed a short time later by Osborn and coworkers [38–42] and some time later by Basset and coworkers [43,44], the compatibility of a multiply bound ligand with an alkylidene set the stage for the development of four-coordinate, fully active, imido alkylidene complexes of tungsten and molybdenum.

There is a close connection between the development of the first well-defined (tungsten) catalysts for alkene metathesis and the discovery of alkylidyne complexes of the type (dimethoxyethane)$Cl_3W≡C\text{-}t\text{-Bu}$ and alkyne metathesis catalysts of the type $(OR)_3W≡C\text{-}t\text{-Bu}$. The trialkoxide compounds (but *not* the trichloride compounds) were found to be highly active for alkyne metathesis and were the first well-defined catalysts for this reaction [45–50]. The expected intermediate alkylidynes or tungstacyclobutadiene species could be observed in alkyne metathesis reactions when bulky electron-withdrawing alkoxides were present, and were isolated and characterized. These studies confirmed that alkoxide ligands promote metathesis-like reactions, while chlorides encourage side reactions that destroy the alkylidyne [51]. On the basis of these studies it was suggested that the most successful W-based olefin metathesis catalyst might be a pseudotetrahedral species that contains sterically demanding alkoxide ligands. Application of alkyne metathesis to organic synthesis is enjoying increased attention today as a consequence of the development of oxidation state W and Mo catalysts analogous to those described above [52–59].

$$\text{(structure)} \quad + \quad \text{(structure)} \quad \xrightarrow{\text{- Ta(O-t-Bu)}_5Cl} \quad \text{(structure)}$$

L = a phosphine

W=C = 2.01 Å; W=O = 1.70 Å
δC_α = 319 ppm; J_{CH} = 121 Hz

(2)

the metal in $W(O)(CH\text{-}t\text{-Bu})Cl_2L_2$ is 18 (assuming a pseudo triple bond is formed between the metal and the oxo ligand) [37], it did not seem likely that it could react with an olefin unless a phosphine or a chloride ligand were lost
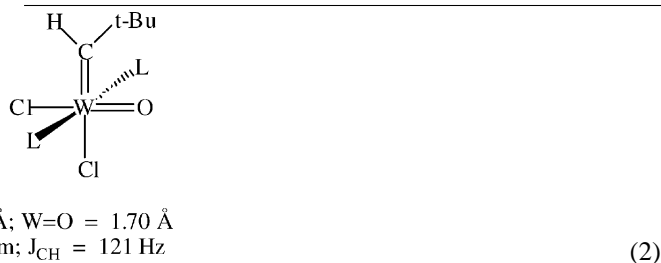
Complexes bearing $N\text{-}2,6\text{-}i\text{-Pr}_2C_6H_3$ (NAr) imido ligands were targeted in order to maximize steric protection at the metal center by the imido group and limit the ability of the imido ligand to bridge between metal centers.

An attractive strategy for the synthesis of W(NAr)(CH-*t*-Bu)(OR)$_2$ species involved alkylidyne complexes. An amido alkylidyne complex, W(NHAr)(C-*t*-Bu)Cl$_2$(dme), was prepared by treating W(C-*t*-Bu)Cl$_3$(dme) with TM-SNHAr. Upon treatment with a catalytic amount of Et$_3$N, W(NHAr)(C-*t*-Bu)Cl$_2$(dme) was transformed quantitatively into W(NAr)(CH-*t*-Bu)Cl$_2$(dme) (Eq. (3)) [60]. Replacement of the chlorides in W(NAr)(CH-*t*-Bu)Cl$_2$(dme) with sterically bulky alkoxides (OR=O-*t*-Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, O-2,6-*i*-Pr$_2$C$_6$H$_3$, etc.) allowed W(NAr)(CH-*t*-Bu)(OR)$_2$ species to be isolated. These should be considered 14-electron complexes, since the imido ligand donates its electron pair to the metal to form a pseudo triple bond. Dimethoxyethane, which binds to the metal only as a chelating ligand, does not remain bound to the metal in the crowded bis(alkoxide) species for steric reasons. The fact that all four ligands in W(NAr)(CH-*t*-Bu)(OR)$_2$ are sterically demanding and covalently attached to the metal center accounts for the compounds' stabilities toward bimolecular decomposition. These catalysts were first reported in 1986 [61].
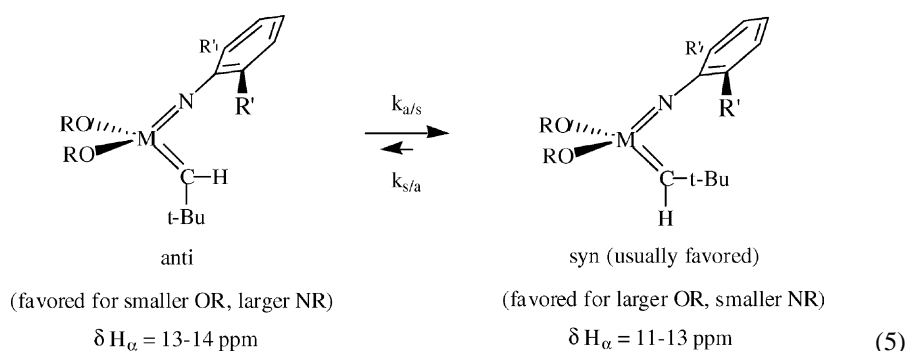

$$(3)$$
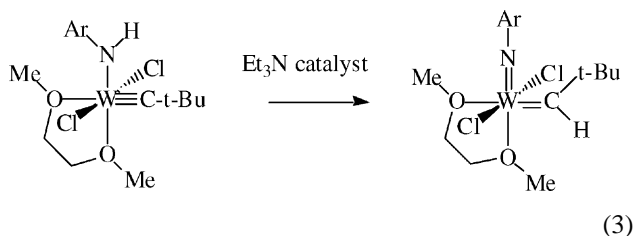
Molybdenum-based catalysts of a type analogous to the tungsten imido alkylidene catalysts were reported in 1987

treatment with three equivalents of triflic acid gives 18-electron Mo(NAr)(CHCMe$_2$R)(OTf)$_2$(dme) (Eq. (4)). In the presence of various alkoxide or aryloxide salts (Li, Na, or K), including even relatively weak

$$(4)$$
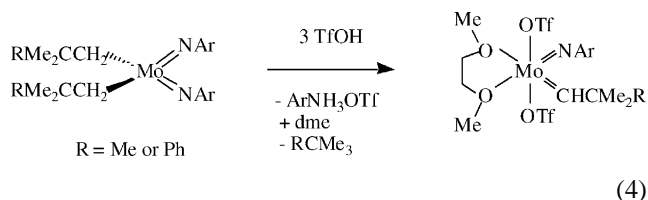
nucleophiles such as LiOCMe(CF$_3$)$_2$, Mo(NAr)(CHCMe$_2$R) (OTf)$_2$(dme) is then converted into Mo alkylidenes Mo(NAr) (CHCMe$_2$R)(OR′)$_2$ [63]. These Mo-based bis(alkoxy)arylimido alkylidenes are stable as long as the alkoxide ligand has sufficient steric bulk to prevent bimolecular decomposition. Lists of stable Mo-based compounds of this type that have been isolated can be found in review articles [15,64,65]. Enantiomerically pure imido alkylidene complexes that contain a biphenolate or binaphtholate ligand were first reported in 1998 [66], and have formed the basis for the development of catalysts for asymmetric olefin metathesis reactions since then [15,16].

An extremely important feature of imido alkylidene complexes (and probably many other types of d^0 M=CHR complexes) is that the alkylidene can exist in two stereoisomeric forms. As shown in Eq. (5), one isomer is the *syn* alkylidene, where the substituent points toward the imido ligand. The other is the *anti* alkylidene, where the substituent points away from the imido

anti

(favored for smaller OR, larger NR)

$\delta\,H_\alpha = 13\text{-}14$ ppm

syn (usually favored)

(favored for larger OR, smaller NR)

$\delta\,H_\alpha = 11\text{-}13$ ppm

$$(5)$$

[62]. However, in order to be practical, an alternative synthesis was required [63]. Toward this end, it was established that Mo(NAr)$_2$(dme)Cl$_2$ can be prepared in large quantities from Na$_2$MoO$_4$, two equivalents of ArNH$_2$, eight equivalents of Me$_3$SiCl, and four equivalents of triethylamine in dimethoxyethane. Alkylation of Mo(NAr)$_2$(dme)Cl$_2$ with neopentyl or neophyl Grignard reagents affords Mo(NAr)$_2$(CH$_2$CMe$_2$R)$_2$, which upon

nitrogen. Studies concerning the structural and reactivity differences of *syn* and *anti* alkylidenes of Mo (largely) and W, and the equilibrium between them, have led to a number of important mechanistic insights into olefin metathesis [15,65]. Although this is a topic of continuing investigation it can be stated simply that although the *syn* isomer is usually the one that is observed in the solid state and that predominates in solution, the *anti* isomer is accessible by rotation about the M=C bond by 180°. The rate of rotation depends heavily upon the nature of the imido and alkoxide

ligands, and can vary by many orders of magnitude, from "slow" (10^{-5} s^{-1}) to "fast" (100 s^{-1}) at room temperature. The reactivities of the two isomers also can vary by many orders of magnitude, although measuring relative reactivities in the case where the interconversion of isomers is fast has been a significant challenge.

Many mechanistic investigations of imido alkylidene catalysts have included modes of decomposition of catalysts. Two primary modes of decomposition have been proposed: (i) rearrangement of metallacyclobutanes to olefins; and (ii) bimolecular decomposition of (most rapidly) methylene complexes [64,67]. Coupling of methylenes was demonstrated most convincingly for 18-electron Cp$_2$(CH$_3$)Ta=CH$_2$ early in the development of high oxidation state alkylidene chemistry [68]. It is believed that an ethylene complex is formed via an intermediate that contains two bridging methylenes [67].

2. Recent studies

In the last several years we have been concerned largely with imido alkylidene complexes of molybdenum that contain chiral biphenolates or binaphtholates and with their efficacy in asymmetric olefin metathesis reactions [15,16]. In addition to 2,6-diisopropylphenylimido and 2,6-dimethylphenylimido catalysts, routes to 2,6-dichlorophenylimido [69] and 1-adamantylimido [70] catalysts have been perfected. Successful catalysts that have been developed contain chiral biphenolates and binaphtholates which are substituted with a bulky alkyl group in the 3 and 3′ positions; catalysts that contain an unsubstituted binaphtholate have never been isolated. The most sterically demanding diolate appears to be a biphenolate substituted with *t*-butyl groups in the 3 and 3′ positions; less sterically demanding are binaphtholates or hydrogenated binaphtholates that contain 2,4,6-triisopropylphenyl, mesityl, or benzhydryl groups in the 3 and 3′ positions. More sterically open catalysts are often isolated as solvent (THF) adducts. They also are sometimes mixtures of *syn* and *anti* isomers. The latter fact, in addition to the fact that THF may bind strongly to one isomer (usually *anti*) and not the other, make crystallization of catalysts difficult. Nevertheless, several crystal structures have been determined in X-ray studies. Two of the most recent are Mo(*N*-2,6-Cl$_2$C$_6$H$_3$)(CH-*t*-Bu)(Biphen)(THF) [69] and Mo(NAdamantyl)(CHCMe$_2$Ph)(Biphen) [70]. THF is found in the former, in spite of the presence of the sterically demanding Biphen ligand, because of the smaller steric demand and greater electron withdrawing ability of the *N*-2,6-Cl$_2$C$_6$H$_3$ ligand. The Mo–C–C angle in each is 150°, which is characteristic of a *syn* isomer in which there is a significant α agostic interaction of the alkylidene's CH$_\alpha$ electrons with the metal. Interestingly, the temperature dependence of the *syn/anti* equilibrium constant for adamantylimido complex [70] differs dramatically from that for an arylimido complex. Typically for an arylimido complex such as Mo(NAr)(CHCMe$_2$Ph)(Biphen) the amount of *syn* isomer decreases as the temperature increases, a process that is controlled largely by the negative value for ΔH (-2.45 kcal mol^{-1}) and the small value for ΔS (-2.65 e.u.) in toluene. In contrast, for Mo(NAd)(CHCMe$_2$Ph)(Biphen) the amount of *syn* isomer ($K_{eq} \sim 200$ at 22 °C) *increases* as the temperature increases, a process that is controlled largely by the relatively *large and positive* value for ΔS (18.03 e.u.), which causes the $-T\Delta S$ term to become significantly larger in absolute value than ΔH (2.30 kcal mol^{-1}) near room temperature. The *syn* isomer is favored in both systems at room temperature, the former for enthalpic reasons, the latter for entropic reasons. Therefore, one might expect dramatically different temperature effects on enantioselectivity for these two species. (This subject that has not yet been investigated in any systematic manner.) The Mo(NAd)(CHCMe$_2$Ph)(Biphen) catalyst has been found to yield enantioselectivities that in some cases differ dramatically from those offered by any arylimido catalyst. The reasons are not yet understood.

The imido groups and diolates that are employed relatively routinely in molybdenum imido alkylidene catalysts
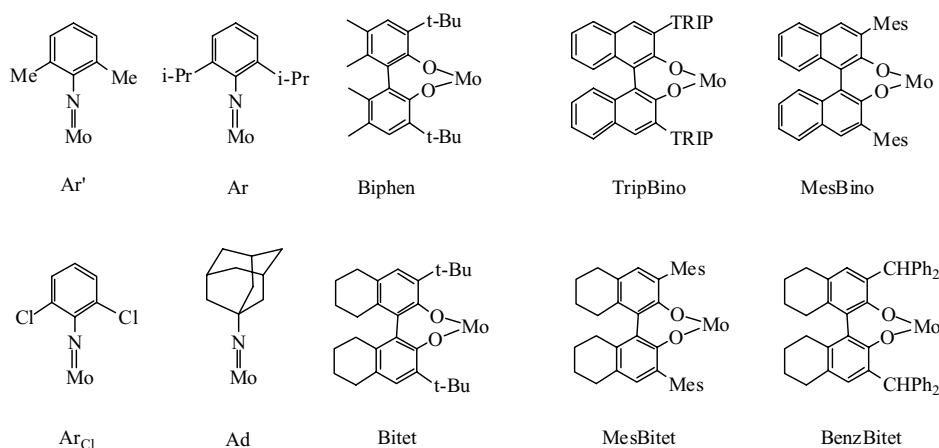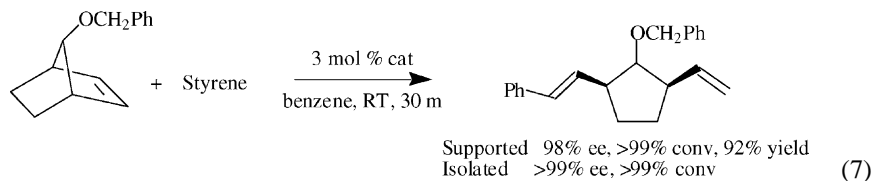

Fig. 1. Imido groups and diolates that are commonly employed to make Mo-based catalysts for enantioselective metathesis reactions.
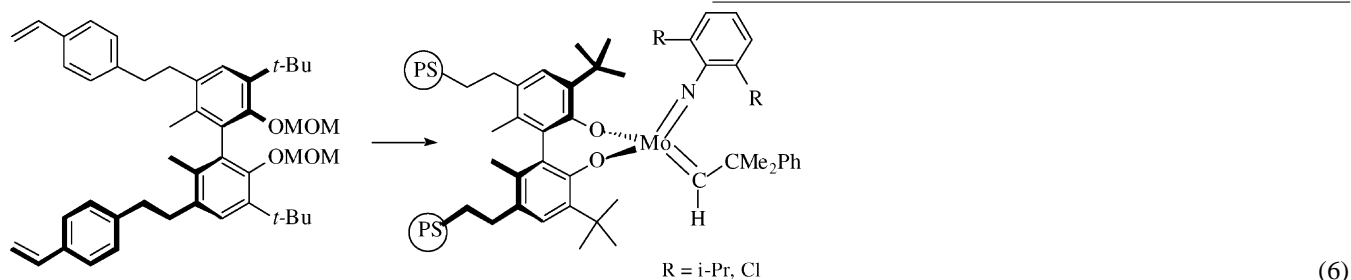
are shown in Fig. 1. Not all 24 combinations have been prepared, and others are known [15]. No "magic catalyst" has been discovered that will achieve high activity and enantioselectivity in all circumstances, and it seems highly unlikely that any will be discovered. Instead, a catalyst must be matched with the desired reaction. The modular nature of the catalysts, therefore, is a significant advantage in terms of

substituted metallacycle formed when ethylene is generated during the reaction are unstable in the long run with respect to rearrangement to yield reduced metal complexes. When no methylene complex is generated during the metathesis reaction, as in the reaction shown in Eq. (7), then the reaction using the supported catalyst is as efficient as that using the catalyst in solution.

$$\text{Supported} \quad 98\% \text{ ee}, >99\% \text{ conv}, 92\% \text{ yield}$$
$$\text{Isolated} \quad >99\% \text{ ee}, >99\% \text{ conv} \tag{7}$$

accomplishing a large variety of enantioselective reactions. Why a given catalyst works for a given type of reaction is still a subject of current investigation. Catalysts have been employed at a level as low as 1%. Temperature and solvent effects on enantioselectivity can be dramatic. Catalyst decomposition, especially of intermediate methylene complexes (if ethylene can be generated during a reaction), takes place over the course of a typical reaction.
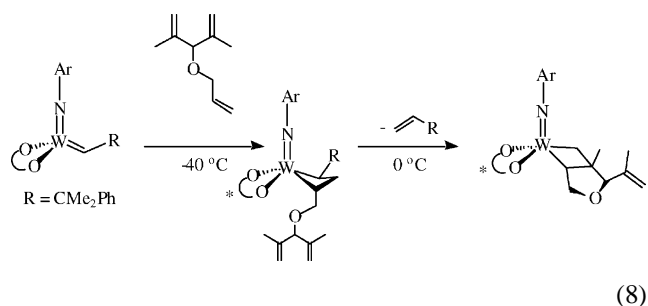
In connection with the development of recoverable and recyclable catalysts, and in the hope that bimolecular decomposition of methylene complexes can be slowed or prevented, catalysts have been prepared that are linked chemically to a polystyrene backbone [71]. A polymerizable Biphen derivative was prepared and polymerized with styrene and divinyl benzene. Deprotection with BBr_3 followed by deprotonation and addition of $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ then produced the supported catalyst shown in Eq. (6). A relatively low percent cross-linking ($\sim$5%) was found

We became interested in whether tungsten-based chiral catalysts could be developed and how they might differ from their molybdenum-based analogs. Two tungsten-based catalysts, $W(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(Biphen)$ and $W(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(Biphen)$, were recently prepared and examined as enantioselective catalysts [72]. They were found to be comparable to the Mo analogs in terms of enantioselectivity, although a higher temperature ($\sim$75 °C) was necessary in order to obtain roughly the same rate, in spite of what is likely to be a higher rate of the fundamental reaction between a tungsten alkylidene and an olefin. The reason for the lower rates is that tungstacyclobutane complexes can form and are relatively stable with respect to dissociation to yield an alkylidene compared to molybdacyclobutane complexes. For example, two intermediate tungstacyclobutane complexes can be observed upon attempting to ring close the substrate shown in Eq. (8). The second tungstacycle rearranged to yield a third relatively stable tungstacycle whose structure is shown in Fig. 2. The

$$R = i\text{-Pr, Cl} \tag{6}$$

to be necessary in order to retain good activity, although in general activity was lower than observed for the analogous homogeneous catalyst. However, the %ee in a typical enantioselective reaction was as high as the %ee for the analogous soluble catalyst. Unfortunately, however, the catalysts were found to be not as long-lived as had been hoped for two reasons. The rate of decomposition of methylene species probably still is relatively high as a consequence of the relatively flexible nature of the lightly cross-linked polystyrene and as a consequence of the relatively high concentration of supported methylenes within the polymer compared to a typical concentration in solution. The second reason is probably because metallacyclobutane species such as the un-

stability of this tungstacycle prevents rapid turnover at room temperature.
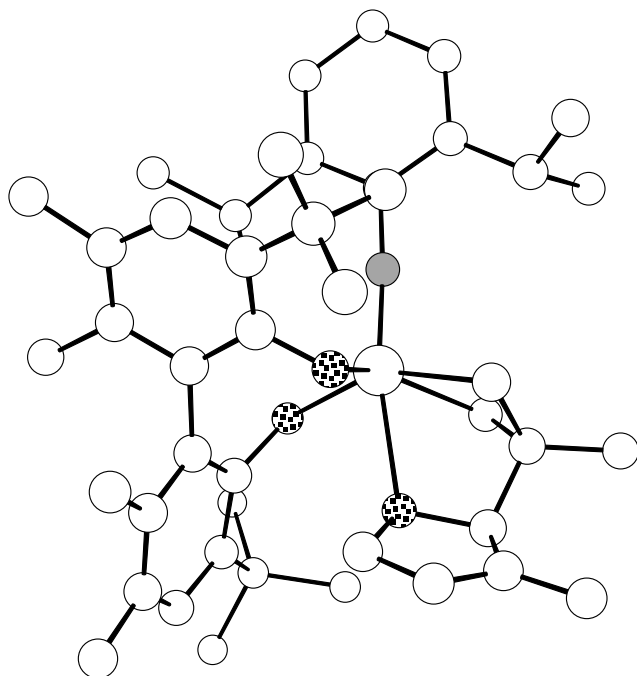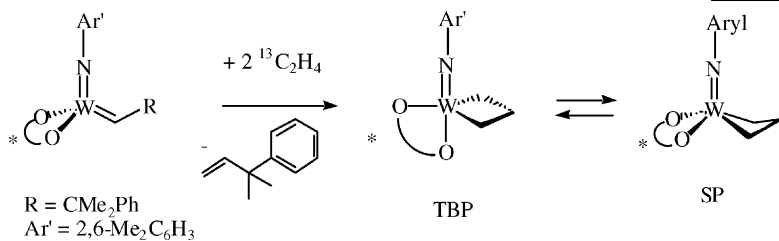

$$R = CMe_2Ph \tag{8}$$

Fig. 2. The final product of the W-catalyzed reaction shown in Eq. (8).

The fact that methylene complexes and unsubstituted metallacyclobutane complexes can form from ethylene that is generated in a metathesis reaction prompted an investigation into the nature of the reactions between the initial neopentylidene or neophylidene complexes and ethylene. The ethylene was ^{13}C-labeled for convenience and reactions were followed largely by ^{13}C NMR methods. Not surprisingly, in the W(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Biphen) system, an unsubstituted tungstenacyclobutane complex (TBP at $-80\,^\circ$C) was observed to form in high yield (Eq. (9)) [72]. Between $-80\,^\circ$C and room temperature a mixture of TBP and SP species was observed. The two types started to interconvert rapidly on the NMR time scale at about $-60\,^\circ$C in a process that did not involve free ethylene, presumably through a five-coordinate rearrangement process. The formation of TBP and SP metallacyclobutane complexes and interconversion of them is well know in the literature [64].

Fig. 3. X-ray structure of Mo(NAr$_{Cl}$)(Bitet)(CH$_2$=CH$_2$)(Et$_2$O).

the basis of the unusually high field chemical shift of the methylene carbon atom, but primarily on the basis of coupling of that carbon to *two* tungsten centers (J_{CW}=36.7 and 78.9 Hz). Since a similar dimer was not observed when the starting W(NAr)(CHCMe$_2$Ph)(Biphen) complex was enantiomerically pure, it was concluded that the dimer contained the two enantiomeric forms of monomeric W(NAr)(CH$_2$)(Biphen). It was also observed that tungstacyclopentane complexes were formed when ethylene added to W(NAr)(CH$_2$CH$_2$)(Biphen), and that these W(NAr)(CH$_2$CH$_2$CH$_2$CH$_2$)(Biphen) species would slowly dimerize ethylene to 1-butene, a type of dimerization that was first documented for tantalacyclopentane

R = CMe$_2$Ph
Ar' = 2,6-Me$_2$C$_6$H$_3$

(9)

Two new species were observed when only 1–1.5 equivalents of ethylene were added to racemic W(NAr)(CHCMe$_2$Ph)(Biphen), an ethylene complex, W(NAr)(CH$_2$CH$_2$)(Biphen), and what appeared to be a dimeric methylene complex, [W(NAr)(CH$_2$)(Biphen)]$_2$ ($\delta C_\alpha = 186$ ppm). The dimeric nature of the latter was established on
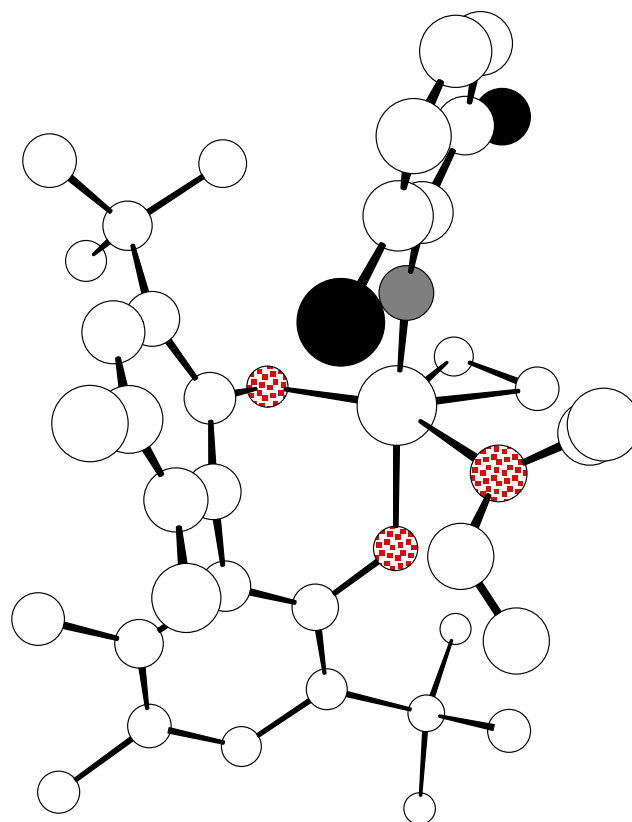
complexes [73]. The ethylene complex could arise either through bimolecular decomposition of a methylene complex or through rearrangement of the unsubstituted tungstacyclobutane complex in the presence of ethylene to give propylene, which was observed in some cases.

Similar observations were made in molybdenum bi-naptholate systems [74] with the following exceptions. No dimeric methylene complexes, ethylene complexes, or molybdacyclopentane complexes were observed.

Reactions between Mo(NAr)(CHCMe$_2$Ph)(Biphen), Mo(NAr$_{Cl}$)(CHCMe$_2$Ph)(Biphen), Mo(NAd)(CHCMe$_2$Ph) (Biphen), or Mo(NAr$_{Cl}$)(CHCMe$_2$Ph)(BenzBitet) and ethylene produced relatively stable ethylene complexes, one of which, W(NAr$_{Cl}$)(CH$_2$CH$_2$)(Biphen)(ether), could be isolated (Fig. 3). In it the ethylene's C–C axis is oriented perpendicular to the Mo=N axis and the C=C bond length was found to be 1.400(13) Å. At high ethylene concentrations the ethylene complexes were found to be in chemically rapid equilibrium with molybdacyclopentane complexes. When only one equivalent of ^{13}C-labeled ethylene was added to Mo(NAr)(CHCMe$_2$Ph)(Biphen),
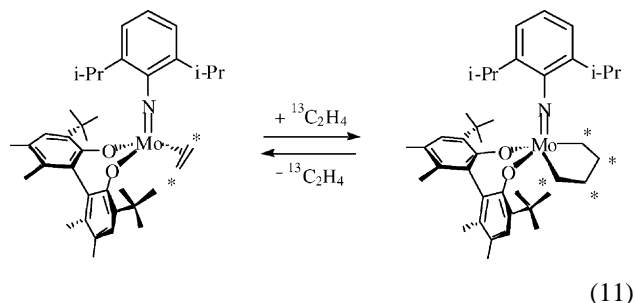
(11)

The possibility of selective cross metathesis [75–77] between a variety of terminal olefins was explored with the hexafluoro-*t*-butoxide and chiral catalysts shown in Fig. 4 [78]. Although no selective cross metatheses stood out, an unusual reaction was discovered in experiments that employed CH$_2$=CHSnBu$_3$. Essentially no cross metathesis was observed between CH$_2$=CHSnBu$_3$ and 1-hexene, although

(one diastereomer)
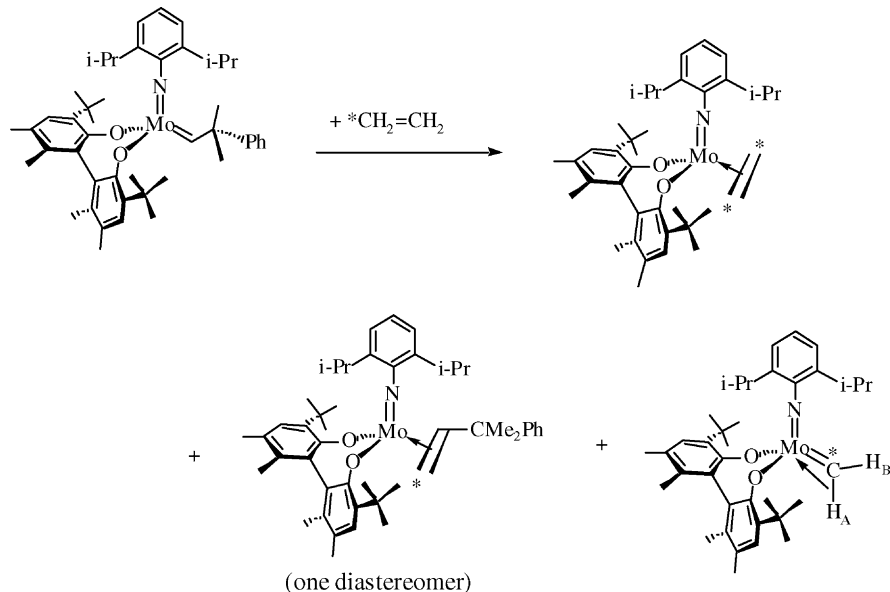
(10)

the complexes shown in Eq. (10) were observed, the last in only trace quantities (δC$_\alpha$ = 253.5 ppm, δH$_\alpha$ = 11.33 (J_{CH} = 134 Hz) and 11.13 ppm (J_{CH} = 163 Hz)). This is the first time that a base-free methylene complex has been observed in solution, although understandably in low concentration relative to other species. With time it decomposed to yield the ethylene complex and other unknown products. Complexes that contain NAd/Biphen and NAr$_{Cl}$/BenzBitet combinations were found to yield similar mixtures. Finally, it was possible to observe the formation of molybda-cyclopentane complexes in equilibrium with the ethylene complex (Eq. (11)) at high concentrations of ethylene (>20 equivalent). The fact that W(VI) tungstacyclopentane complexes are formed more readily than Mo(VI) molybda-cyclopentane complexes can be understood in terms of the greater ease of oxidation of W versus Mo.

homometathesis products of 1-hexene (5-decenes) were observed. However, CH$_2$=CHSnBu$_3$ was consumed to yield a mixture of CH$_2$=CHCH$_2$SnBu$_3$, Bu$_3$SnCH=CHCH$_2$SnBu$_3$, and Bu$_3$SnCH$_2$CH=CHCH$_2$SnBu$_3$. The first two of these products are unusual in that they contain an odd number of carbons; the last is a homocoupling product of the first. We found that it was possible to use an ethylene complex as a catalyst, as shown in Eq. (12). NMR studies revealed that Mo(NAr)(CH$_2$=CHSnBu$_3$)(Biphen) was formed readily from Mo(NAr)(CH$_2$=CH$_2$)(Biphen). On the basis of studies involving tantalacyclopentane complexes to be described below, we speculate that the allyltin product is formed via the "ring-contraction" mechanism shown in Eq. (13). Beta hydride elimination (and readdition) in the mixed molybda-cyclopentane takes place selectively at the position β to tin and Mo, but once the
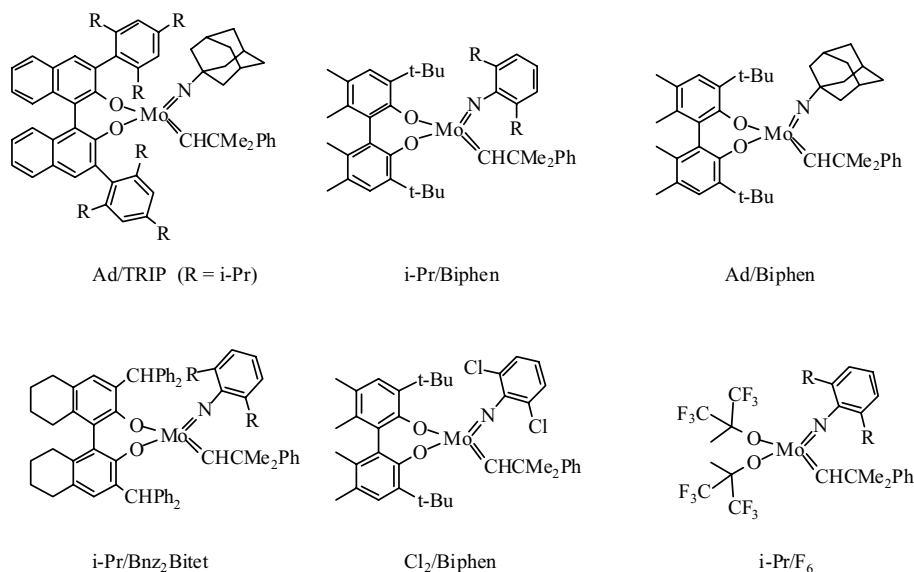
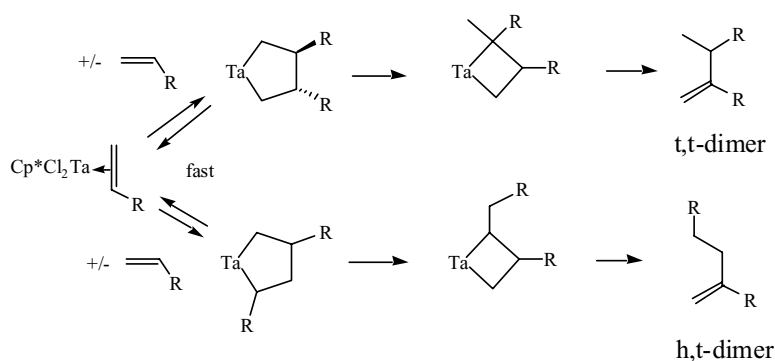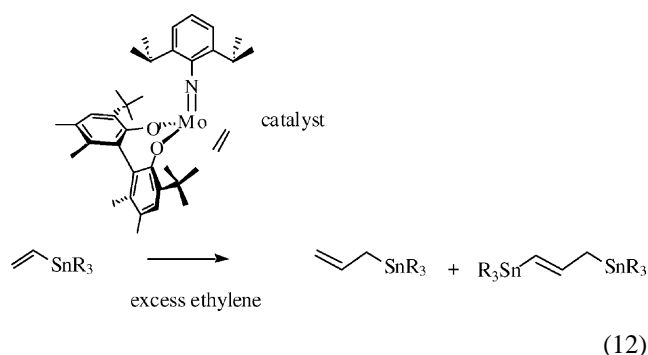Fig. 4. Catalysts explored for cross-metathesis.

Fig. 5. Mechanism of dimerization of propylene by tantalum catalysts.

(12)

α substituent becomes a carbon atom, then rearrangement is slow with respect to metathesis to give the methylene complex. At this stage it is not known whether the methylene complex reacts with $CH_2=CHSnBu_3$ to give more $CH_2=CHCH_2SnBu_3$ via rearrangement of an α-substituted molybdacyclobutane, or whether the methylene species decomposes to yield $Mo(NAr)(CH_2=CH_2)(Biphen)$. If the system contains a deficiency of ethylene, then the molybdacyclopentane shown in Eq. (14) forms and gives rise to $Bu_3SnCH=CHCH_2SnBu_3$ in a similar ring-contraction mechanism. Although these results are preliminary, it seems almost certain that the odd carbon products are


(13)
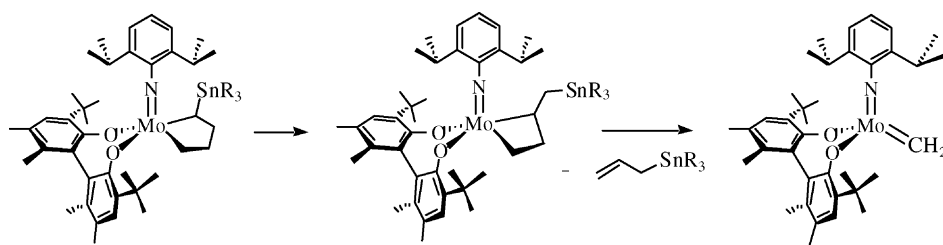
formed in ring-contractions that are "interrupted" with a metathesis step.
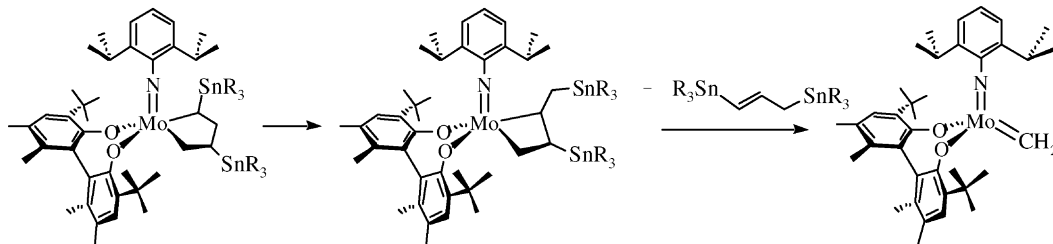
(14)

The ring-contraction mechanism was first proposed in 1979 [79–81] in order to account for the deuterium labeling found in olefin dimers formed catalytically from tantalacyclopentane complexes (Fig. 5). Bergman proposed a similar ring-contraction in 1985 for the result shown in Eq. (15) [82]. Therefore, one might expect ring-contraction to be seen for Mo or W complexes in the right circumstances.
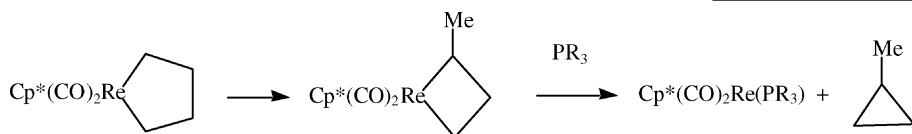
(15)

The most unusual feature of the Mo-catalyzed ring-contraction is that a high oxidation state methylene complex is formed from a Mo(IV) complex. In theory, therefore, it may be possible to generate metathesis catalysts from reduced metal complexes in this fashion. In fact, this possibility was recognized in the 1979 tantalum paper, viz. "the MC_4 to MC_3 ring contraction is a straightforward and reasonable way of forming an alkylidene ligand from olefins . . . when no alkylating agent is present." The details of this unusual reaction remain to be worked out, but at this stage there is no competitive mechanism in the offing. We are also curious whether other vinyl compounds (e.g., Si) behave similarly, whether ordinary olefins can be homologated by certain metals in this manner, and whether tungsten is a more effective catalyst for such reactions than molybdenum.

3. Conclusions and future outlook

The journey from a new high oxidation state Ta alkylidene complex to well-defined W and Mo imido alkylidene catalysts for the metathesis of olefins required approximately 15 years. A crucial finding was that bulky alkoxide ligands slow the rearrangement of tantalacyclobutane rings to olefins and promote olefin metathesis. Bulky alkoxide ligands, especially electron-withdrawing ones, also were found to promote acetylene metathesis reactions catalyzed by high oxidation state W or Mo alkylidyne complexes. Throughout this journey, however, the principle of preventing bimolecular decomposition with sterically demanding ligands covalently bound to the high oxidation state metal has been the guiding light.

The issues we have addressed most recently concern the production and decomposition of methylene complexes (which are unstable toward bimolecular decomposition as a consequence of the small size of the methylene ligand), the preparation of tungsten catalysts, and the nature of the ultimate decomposition product or products in the presence of ethylene. Most interestingly, we have found hints that d^2 metal complexes (e.g., Mo(IV) and W(IV)) may not be dead ends in all circumstances, i.e., alkylidenes may be regenerated from them. Whether or not metathesis of ordinary olefins can be initiated by the olefins themselves in a well-defined catalyst system remains to be seen.

A question that often arises is whether olefin metathesis catalysts can be developed that are not d^0 species containing Mo, W, or Re, or that are not "Ru(II)" species of the type first prepared by Trnka and Grubbs [83]. Of course there is always a possibility that other types of catalysts eventually will be prepared, although in view of the effort required to develop the known well-defined catalysts, it is difficult to concede at this point in time that some opportunity has been overlooked. However, further refinements of known systems still present many opportunities to which we can look forward in the future.

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